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End-functionalized polymers by living cationic polymerization

2. Vinyl ether macromers with a poly(vinyl ether) backbone

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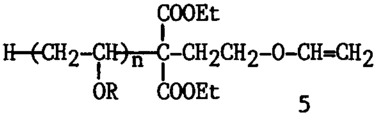
SUMMARY

Living polymers of isobutyl and 2-benzoyloxyethyl vinyl ethers, initiated by the hydrogen iodide/iodine system, were cleanly end-capped with the sodium salt of diethyl 2-vinyloxyethylmalonate [$Na^{\oplus\ominus}C(COOEt)_2CH_2CH_2OCH{=}CH_2$] to give new macromers (5) consisting of a vinyl ether terminal and a monodisperse poly(vinyl ether) backbone ($\bar{M}_w/\bar{M}_n < 1.1$). Their perfect end-functionality ($\bar{F}_n \cong 1.0$) was established by ^1H- and ^{13}C-NMR structural analysis. Macromers 5 could copolymerize with alkyl vinyl ethers under cationic conditions.



$$\mathrm{H\!\left(CH_2-\underset{OR}{CH}\right)_{\!n}\underset{COOEt}{\overset{COOEt}{C}}-CH_2CH_2-O-CH{=}CH_2}$$

5

5a: R = $CH_2CH(CH_3)_2$
5b: R = $CH_2CH_2OCOC_6H_5$

INTRODUCTION

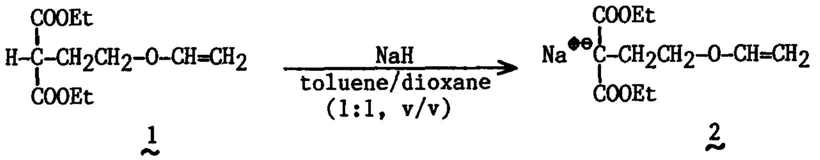
Cationic polymerization of vinyl ethers offers at least two synthetic advantages: First, these monomers give well-defined monodisperse living polymers when polymerized by the hydrogen iodide/iodine (HI/I_2) initiating system (1-3). Second, a variety of functional groups can readily be introduced into their alkoxyl pendants; the living polymerization by HI/I_2 is not adversely affected by the pendent functional groups (4-11). The most recent example of such "functionalized" vinyl ethers is diethyl 2-vinyloxyethylmalonate (1; eq 1) with a malonic ester in the pendant (10,11).

Noting these advantages, we have synthesized, in the first study of this series (10), terminally mono- and bifunctional poly(vinyl ether)s with malonic ester or carboxylic acid end-groups. In one example, the malonate-capped polymers were prepared by end-capping a living poly(vinyl ether) with the malonate anion $^{\ominus}CH(COOEt)_2$. Another method involves the HI adduct of vinyl ether 1 as a functional initiator for living polymerization of vinyl ethers.

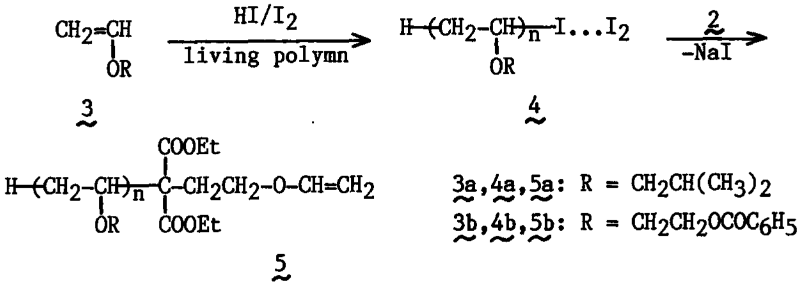
This study is to extend the combination of our living polymerization of vinyl ethers and the clean end-capping by the malonate anion to the synthesis of new macromers (5) that consist of a vinyl ether terminal and a monodisperse poly(vinyl ether) backbone (eqs 1 and 2). By the use of the same living process, we have recently obtained poly(vinyl ether) macromers with a methacrylate terminal (8), but the methacrylate group was introduced by a functional initiator method, rather than by end-capping. Although a number of macromers have already been prepared (12), almost none carry a vinyl ether terminal polymerizable by a cationic mechanism.

As illustrated in eqs 1 and 2, we utilized the malonate-containing vinyl ether 1 as the precursor of malonate-type anion 2 in which the vinyl ether function of 1 is kept intact (eq 1). Functional anion 2 was in turn allowed to terminate the HI/I_2-initiated living polymers (4) of vinyl ether 3 (eq 2). Selective end-capping of 4 with 2 led to macromers 5 with perfect end functionality.

For the backbone of 5, isobutyl vinyl ether (IBVE; 3a) (1,2) and 2-benzoyloxyethyl vinyl ether (BzOVE; 3b) (4) were used, both of which undergo living cationic polymerization in the presence of the HI/I_2 initiator. IBVE, an alkyl vinyl ether, gives macromer 5a with a lipophilic branch; the ester-containing poly(BzOVE) backbone of 5b can readily be hydrolyzed into a hydrophilic (water-soluble) polyalcohol $\mathrm{+CH_2{-}CH(OCH_2CH_2OH){+}_n}$ (4,5).



$$\underset{\mathbf{1}}{\mathrm{H{-}C(COOEt)_2{-}CH_2CH_2{-}O{-}CH{=}CH_2}} \xrightarrow[\text{toluene/dioxane (1:1, v/v)}]{\text{NaH}} \underset{\mathbf{2}}{\mathrm{Na^{\oplus}\,{}^{\ominus}C(COOEt)_2{-}CH_2CH_2{-}O{-}CH{=}CH_2}} \qquad (1)$$



$$\underset{\mathbf{3}}{\mathrm{CH_2{=}CH(OR)}} \xrightarrow[\text{living polymn}]{\mathrm{HI/I_2}} \underset{\mathbf{4}}{\mathrm{H{+}CH_2{-}CH(OR){+}_n I\cdots I_2}} \xrightarrow[\mathrm{-NaI}]{\mathbf{2}} \underset{\mathbf{5}}{\mathrm{H{+}CH_2{-}CH(OR){+}_n C(COOEt)_2{-}CH_2CH_2{-}O{-}CH{=}CH_2}} \qquad (2)$$

3a,4a,5a: R = $\mathrm{CH_2CH(CH_3)_2}$
3b,4b,5b: R = $\mathrm{CH_2CH_2OCOC_6H_5}$

EXPERIMENTAL

Materials

Diethyl 2-vinyloxyethylmalonate 1 was synthesized from 2-chloroethyl vinyl ether and ethyl malonate as reported (10). IBVE was commercially obtained, washed with 10% aqueous sodium hydroxide solution and then with water, and dried over anhydrous sodium sulfate. BzOVE was prepared by the reaction of 2-chloroethyl vinyl ether with sodium benzoate (3,4). These vinyl ethers were then purified by double distillation (under reduced pressure for 1 and BzOVE) over calcium hydride before use; gas-chromatographic purity $\geq$ 99.5% for each monomer. Solvents (toluene and methylene chloride) were purified by the usual methods (1) and distilled over calcium hydride at least twice before use.

The stock solution (0.224 M) of anion 2 (as sodium salt) was obtained by treating 1 (1.07 mL, 4.7 mmol) with sodium hydride (60 wt% dispersion in mineral oil, 0.189 g, 4.7 mmol) in a toluene/dioxane mixture (10 mL/10 mL) at ca. 40°C under dry nitrogen. This was kept under dry nitrogen at -25°C and used directly for end-capping.

Procedures

Living cationic polymerizations of IBVE and BzOVE by HI/I_2 were carried out at -15°C under dry nitrogen, as reported previously (1), and terminated with 2 (5-fold molar excess over the living ends). Conversions of

IBVE and BzOVE were determined by gas chromatography. The quenched reaction mixture was filtered to remove the sodium iodide precipitate, washed with 10% aqueous sodium thiosulfate solution and then water, evaporated to dryness under reduced pressure, and dried in vacuo. The polymers thus recovered were separated from unreacted quencher **2** by preparative size-exclusion chromatography (SEC) (Jasco Megapak 201 polystyrene gel) in chloroform.

Cationic copolymerizations of macromers **5** with IBVE were run in a similar manner (initiators: HI/I_2 and boron trifuoride etherate), except that they were terminated with prechilled methanol containing a small amount of ammonia.

The molecular weight distribution (MWD) and number-average molecular weight ($\bar{M}_n$) of the polymers were determined by SEC on the basis of a polystyrene calibration (1). ^1H and ^{13}C NMR spectra (90 and 22.5 MHz, respectively) were measured in $CDCl_3$ at room temperature on a Jeol FT-90Q instrument.

RESULTS AND DISCUSSION

Synthesis of Macromer 5a from Isobutyl Vinyl Ether

According to the synthesis route outlined in eqs 1 and 2, IBVE was first polymerized by HI/I_2 initiator in methylene chloride at -15°C (conversion of IBVE = ca. 100%) (2), and the resulting living polymer **4a** was treated with a 5-fold molar excess of anion **2**. The living end reacted instantaneously with the quencher, as indicated by the immediate precipitation of sodium iodide.

Figure 1 shows a typical ^1H NMR spectrum (Fig. 1b) of the products along with the spectrum (Fig. 1a) of vinyl ether **1** as the precursor of the end-capping agent **2**. In addition to the absorptions due to the poly(IBVE) backbone (peaks i-m) and its head methyl group (peak g), Figure 1b exhibits the signals of the end group originating from **2**, such as peaks a and b for the vinyl ether moiety, c and d for the spacer methylenes, and e and f for the ethyl groups of the malonic ester. These assignments were confirmed by comparing Figures 1a and 1b; no evidence was found for reactions and polymerization of the vinyl ether function of the quencher **2**.

^{13}C NMR structural analysis of the products also showed the attachment of a vinyl ether group to the polymer terminal: δ170.8 (C=O), 151.5 (=CH), and 86.4 (=CH_2); the corresponding absorptions of **1**: δ168.8 (C=O), 151.2 (=CH), and 86.5 (=CH_2) (10). Thus, the end-capping of living poly(IBVE) with the malonate-type anion **2** led to macromer **5a** (eq 2).

The end functionality of **5a** was determined by ^1H NMR spectroscopy. Namely, in Figure 1b, the integrated area of peak b ($-\underline{CH}=CH_2$), relative to those of the main-chain protons (δ2.9-3.8, peaks h, j, and k), gave the amount (in mol/L) of the terminal vinyl groups. Figure 2 plots these [CH_2=CH-O-] values as a function of the initial concentration ($[HI]_0$) of hydrogen iodide, which is in turn equal to the concentration of living ends (3). All the plots fall on the diagonal of Figure 2, showing that [CH_2=CH-O-] = $[HI]_0$ = [living end]; i.e., each polymer chain carries one vinyl ether terminal.

Another feature of macromer **5a** is its narrow MWD with $\bar{M}_w/\bar{M}_n < 1.1$ over the whole range of $[HI]_0$ employed (Fig. 2). The narrow MWD means that reaction 2 affords macromers not only with perfect end functionality ($\bar{F}_n \cong 1.0$) but with controlled molecular weight as well.

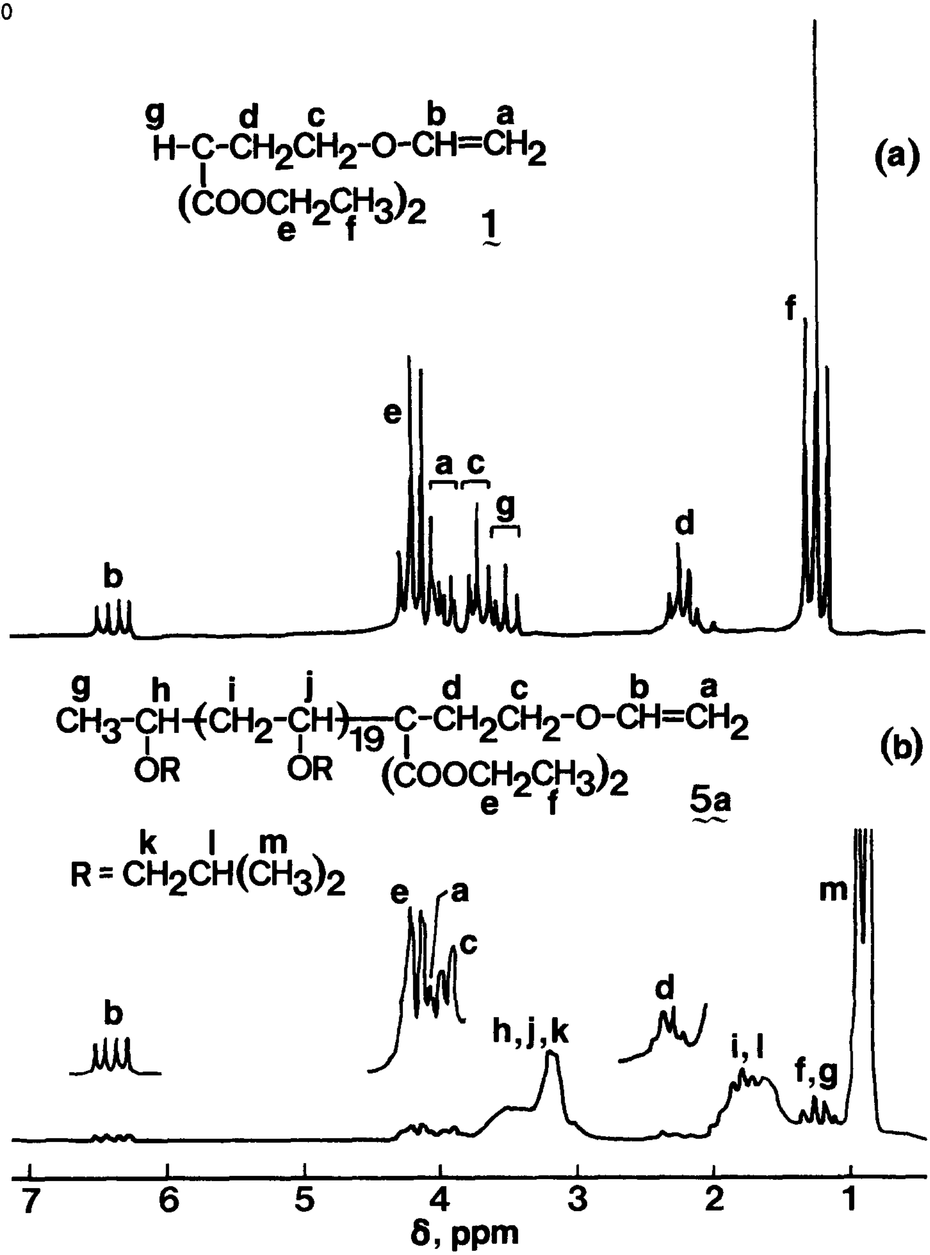


Figure 1. ^{1}H NMR spectra of (a) diethyl 2-vinyloxyethylmalonate (1) and (b) macromer 5a. Synthesis conditions for 5a: $[\mathrm{IBVE}]_0 = 0.38$ M, $[\mathrm{HI}]_0 = 18$ mM, $[\mathrm{I_2}]_0 = 0.20$ mM; CH_2Cl_2 solvent, −15°C; t = 12.5 min, IBVE conversion = 95%; $\bar{M}_n = 2300$ (by SEC), $\bar{M}_w/\bar{M}_n = 1.06$.

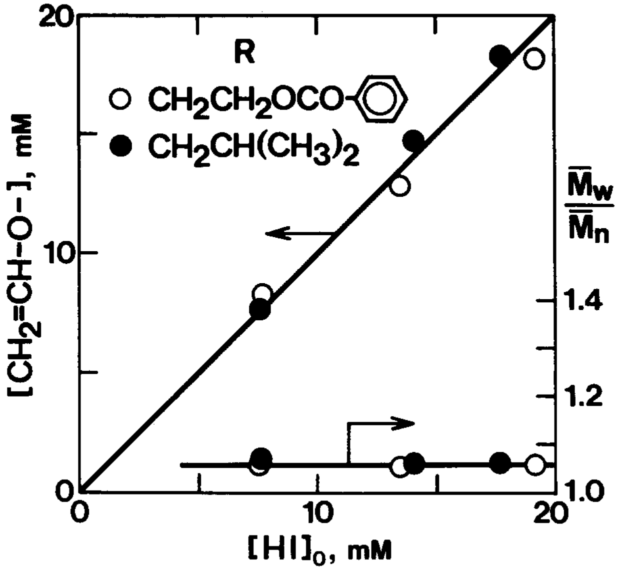


Figure 2. $[CH_2=CH-O-]$ and $\bar{M}_w/\bar{M}_n$ values for macromers 5a and 5b as a function of $[HI]_0$ (= [living end]): (●) 5a, $[IBVE]_0 = 0.38$ M, $[I_2]_0 = 0.20$ mM, CH_2Cl_2 solvent, -15°C, IBVE conversion = 93-96%; (○) 5b, $[BzOVE]_0 = 0.28$ M, $[I_2]_0 = 5.0$ mM, toluene solvent, -15°C, BzOVE conversion = 71-98%.

Synthesis of Macromer 5b from 2-Benzoyloxyethyl Vinyl Ether

Reaction 2 was also applicable to BzOVE. The HI/I_2-initiated living polymerization of BzOVE was carried out in toluene at -15°C (4), and subsequently terminated with a 10-20-fold molar excess of 2 when the reaction was almost completed. Immediate precipitation of sodium iodide ensued, indicating rapid quenching of the living ends.

^1H NMR structural analysis (Fig. 3) of the products established the formation of macromer 5b. For example, Figure 3 exhibits the absorptions of the terminal group: peaks a and b ($CH_2=CH-O-$); c and d (OCH_2CH_2); and e and f ($COOCH_2CH_3$). The other signals, typically m and n in the aromatic region, are assignable to the poly(BzOVE) backbone. The vinyl ether terminal was also observable by ^{13}C NMR: δ169.4 (C=O); 151.3 (=CH); and 86.5 ($=CH_2$).

The peak intensity ratio, b/(m+n) = [=CH-O-]/[aromatic H], gave the $[CH_2=CH-O-]$ values (in mol/L) for macromer 5b, and they are plotted against $[HI]_0$ in Figure 2. The fact that $[CH_2=CH-O-] = [HI]_0$ = [living end] shows the existence of one terminal vinyl ether function per chain ($\bar{F}_n \cong 1.0$). Figure 2 also shows the MWD of 5b to be very narrow ($\bar{M}_w/\bar{M}_n < 1.1$), and hence its molecular weight to be controllable by the monomer-to-initiator feed ratio.

The pendent ester groups of macromer 5b can be hydrolyzed under basic conditions after the cationic polymerization of its vinyl ether terminal (eq 3). The hydrolysis product 7 is an amphiphilic graft polymer which consists of a lipophilic poly(alkyl vinyl ether) backbone and hydrophilic poly(hydroxyethyl vinyl ether) grafts, both being connected via a malonic acid junction.

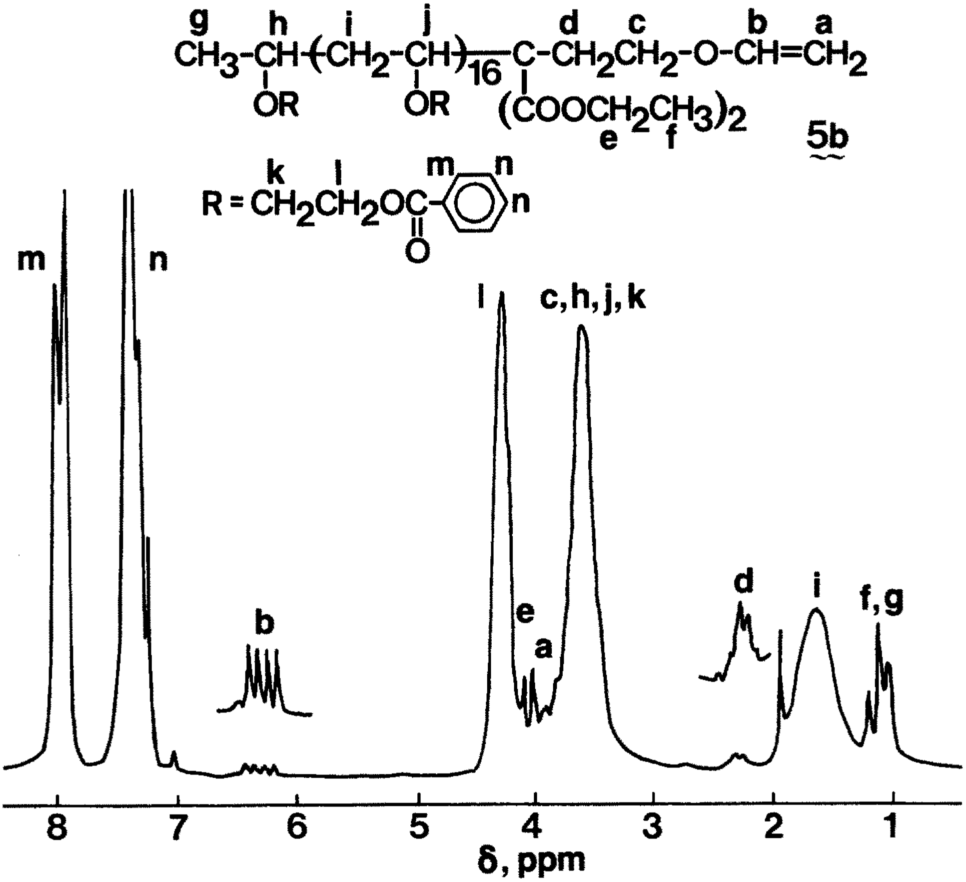
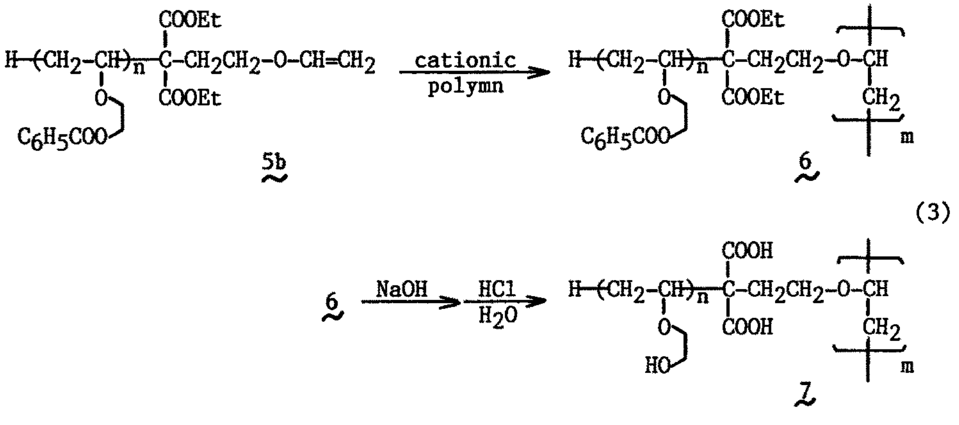


Figure 3. ^{1}H NMR spectrum of macromer 5b. Synthesis conditions: $[BzOVE]_0$ = 0.28 M, $[HI]_0$ = 14 mM, $[I_2]_0$ = 5.0 mM; toluene solvent, -15°C; t = 153 min, BzOVE conversion = 89%; $\bar{M}_n$ = 3000 (by SEC), $\bar{M}_w/\bar{M}_n$ = 1.06.



(3)

Cationic Polymerization of Macromers 5a and 5b

Preliminary experiments showed that the vinyl ether moieties of **5a** and **5b** could be homo- and copolymerized by cationic initiators such as boron trifluoride etherate and HI/I_2 (cf. eq 3). For example, copolymerization of **5b** ($\bar{M}_n$ = 2500 by SEC, $\bar{M}_w/\bar{M}_n$ = 1.07) with IBVE readily proceeded with HI/I_2 as initiator in methylene chloride at $-15^{\circ}C$ ($[\mathbf{5b}]_0$ = 19 mM, $[IBVE]_0$ = 200 mM, $[HI]_0$ = 9.5 mM, $[I_2]_0$ = 0.22 mM), to give graft polymers; conversions of **5b** and IBVE were both 100% in 15 min. Detailed investigations in this line are now in progress.

REFERENCES

1. M. Miyamoto, M. Sawamoto, and T. Higashimura, *Macromolecules*, **17**, 265, 2228 (1984).
2. T. Enoki, M. Sawamoto, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 0000 (1986).
3. As reviews, see: (a) T. Higashimura and M. Sawamoto, *Adv. Polym. Sci.*, **62**, 49 (1984). (b) *Idem*, *Makromol. Chem., Suppl.*, **12**, 153 (1985). (c) *Idem.*, *ibid.*, in press.
4. (a) T. Higashimura, S. Aoshima, and M. Sawamoto, *Makromol. Chem., Suppl.*, in press. (b) S. Aoshima, T. Nakamura, M. Sawamoto, and T. Higashimura, *Polym. Prepr., Jpn.*, **34**, 169 (1985).
5. S. Aoshima, T. Nakamura, N. Uesugi, M. Sawamoto, and T. Higashimura, *Macromolecules*, **18**, 2097 (1985).
6. S. Aoshima, O. Hasegawa, and T. Higashimura, *Polym. Bull.*, **13**, 229 (1985).
7. S. Aoshima, O. Hasegawa, and T. Higashimura, *Polym. Bull.*, **14**, 417 (1985).
8. S. Aoshima, K. Ebara, and T. Higashimura, *Polym. Bull.*, **14**, 425 (1985).
9. T. Nakamura, S. Aoshima, and T. Higashimura, *Polym. Bull.*, **14**, 515 (1985).
10. M. Sawamoto, T. Enoki, and T. Higashimura, *Macromolecules*, in press.
11. M. Sawamoto, T. Enoki, and T. Higashimura, *Polym. J.*, in preparation.
12. As a recent review, see: P. F. Rempp and E. Franta, *Adv. Polym. Sci.*, **58**, 1 (1984).

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